Morphological Investigation of Liquid Crystal/Polymer Mixtures Induced by Patterned Ultraviolet Light

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The morphology of polymer-walls in liquid crystal/monomer mixtures, produced by irradiating selective areas of a cell with non-uniform ultraviolet (UV) light irradiation through a photomask to induce phase separation by photopolymerization, have been investigated using both optical and scanning electron microscopy. It was found that it is possible regulate the morphology of the polymer-walls by controlling the photopolymerization process which occurs during curing in two-phase region. The mechanisms of polymer-wall formation are complex, including local photopolymerization and diffusion processes.

Keywords: liquid crystal device, photopolymer, polymerization-induced phase separation, polymer wall, diffusion model

1. Introduction

Liquid crystal/polymer composites are a relatively new class of materials which have been of great interest for various electro-optical applications [1,2], such as displays [3,4], light shutters [5], switchable windows [6], tunable lenses [7], optical switches for telecommunication [8,9], switchable photonic crystals [10], and optical data storage.[11] These composite systems may appear in network or droplet form, depending on the polymer and concentration used. They consist of low molecular weight liquid crystals (LCs) and polymers, and can be divided into two subsystems: polymer dispersed liquid crystals (PDLC) and polymer stabilized liquid crystals (PSLC; also known as 'liquid crystal gel'). [1,2] These heterogeneous systems are generally prepared via phase separation induced by thermal quenching [12], solvent removal [13–15], and thermally or photo-chemical initiated polymerization.[13,16–19]

Of these methods, polymerization-induced phase separation (PIPS) initiated by ultraviolet (UV) radiation is a preferred way of producing these composites because of the ease of the fabrication process, requiring no solvent. [17–19] These composites have been customarily prepared via PIPS under uniform UV irradiation to obtain uniform distributions of LC droplets in a continuum of cross-linked polymer.

Recently, another type of composite system, possessing polymer wall structure, has been developed using patterned PIPS of LC/monomer mixtures. The formation of polymer walls was achieved by irradiating selective areas of a cell with non-uniform UV light through a photomask to induce phase separation by photopolymerization. This method was demonstrated in the formation of polymer walls for the fabrication of an axially symmetric aligned microcell (ASM) [20], a polymer matrix supertwisted nematic LC [21],

and a bistable cholesteric mixture.[22] Polymer walls have also been formed successfully in ferroelectrics LC and π -cells.[23,24] The polymer-walls in the inter-pixel regions not only improve the electro-optic characteristics of LC/polymer devices, but also provide excellent pressure resistance, preventing distortion of a display image. Furthermore, these LC devices with polymer-walls can be used to form self-adhering films, with self-sustaining structure, on flexible substrates. No vacuum filling process is needed during the cell fabrication. These polymer walls provide rigid supports for the top and bottom substrates and provide a uniform cell gap.

The electro-optic performance of a polymer wall structured LC will obviously depend on the wall structure and morphology. In order to optimize the electro-optical performance, it is important to understand and control the wall formation process. This paper, addresses the morphology development and phase separation dynamics. Using the LC/monomer phase diagram as a guide to photopolymerization, the effects of temperature and LC concentration on the emergence of the domain morphology of the composites have been examined. The morphology of the polymer wall has also been investigated using scanning electron microscopy (SEM) after removal of the LC using an appropriate solvent. Finally, the mechanism of a local photopolymerization-induced phase separation using non-uniform UV irradiation and structure formation is elucidated in terms of the temporal evolution of morphology and structure.

2. Experimental

2.1 Materials

The photopolymerizable optical adhesive (NOA73, supplied by *Norland Products Inc.*) was used as the prepolymer material. NOA73 has a low viscosity of 140 cps and has the form of a multifunctional acrylate monomer that will cure when exposed to UV light with a wavelength of 350-380nm. The liquid crystal used was a nematic mixture (JB-5002 $\times\times$, supplied by *Chisso Corp.*), possessing positive dielectric anisotropy ($\Delta\epsilon = 9.0$, $\epsilon_{\perp} = 4.2$, $\epsilon_{\parallel} = 13.2$), high birefringence ($\Delta n = 0.203$, $n_o = 1.515$, $n_e = 1.718$), a low viscosity of 30.6 cps at 20°C, and a nematic-isotropic transition

temperature of 83.4°C.

2.2 Phase Diagram of LC/Monomer Mixtures

Regarding the establishment of the phase diagram and the investigation of morphology development and phase separation dynamics, several LC/monomer mixtures were prepared by weighing desired amounts of NOA73 and JB-5002 $\times\times$ in small vials and then mixing by stirring vigorously using a magnetic stirrer. For the optical microscopy experiment, a polarizing microscope (model ECLIPSE E600POL, supplied by *Nikon Corp.*) was used. A sample hot stage (model TS62, supplied by *INSTECH* was used), interlinked to a programmable temperature controller (model STC200, supplied by *INSTECH*). Mixtures were sandwiched between two glass substrates, then heated until they were optically isotropic, and then cooled slowly at a rate of -1 °C/min. The temperature of phase change was monitored under the optical microscope equipped with a digital camera (model DXM1200, supplied by *Nikon Corp.*).

2.3 Preparation of LC/Polymer Composites

In this study, a photopolymerization-induced phase separation method was used to prepare π -cells with polymer walls from JB-5002 $\times\times$ and NOA73.[24] Figure 1 shows the process that was used to fabricate a device with polymer-walls. Homogeneous mixtures of 92 wt% of JB-5002 $\times\times$ and 8 wt% of NOA73 were introduced into the thin gap between two glass substrates, which had been coated with indium-tin-oxide (ITO) electrodes. The dimension of the gap was set by inserting 5 μ m plastic spacers between the plates. The substrates that were used in this cell were coated with polyimide alignment layers (SE7759, supplied by *Nissan Chemical Industries, Ltd.*) that were rubbed in parallel directions, to produce a pre-tilt angle of about

Fig. 1. Fabrication process for an LC cell with polymer-walls.

7 degrees for the LC molecules. The cells were capillary-filled at 100°C, at which temperature the formulated mixture was in the isotropic phase. The phase separation temperature of the liquid crystal/monomer (92/8) formulation was 68°C, as observed during the cooling using a cross-polarizing optical microscope in transmission mode.

After filling, the homogeneous mixtures in the cells were cooled down to induce phase separation. The phase separation occurring in the mixture changes from an isotropic, homogeneous state to a heterogeneous state upon cooling, including a nematic-rich phase and a monomer-rich phase. Finally, the mixture is exposed to 365nm wavelength through an external photomask with a lattice pattern, in which the line widths and spacing were approximately of 20 and 500 μm , respectively. The curing UV intensity, corresponding to the photomask, has the form of a spatially non-uniform and periodic rectangular pattern along the x -direction, but is uniform along the y -direction, as shown in Fig. 1. This patterned photopolymerization reaction, induced by the non-uniform light intensity, can form spatial variations in the structure, i.e. polymer walls in LC.

2.4 Examination of Morphology of LC/Polymer Composites

Morphological pictures were acquired under polarized light by means of an optical microscope equipped with a digital camera. A scanning electron microscope (SEM) was used to examine the morphology of the polymer walls. To prepare a sample for SEM measurement, a cured cell containing the LC/polymer composite was immersed in methanol for one hour and then disassembled. The substrate was then rinsed with methanol to extract the LC while leaving the polymer wall domains intact, as they are no longer soluble in methanol. The glass substrate containing the polymer wall was cut to an appropriate size to fit the geometry of the SEM sample holder. The morphology of the polymer walls was then examined using SEM (model VE-7800, supplied by KEYENCE Corp.). The emerging morphology was examined as a function of temperature and UV light intensity.

3. Results and Discussion

3.1 Phase Diagram of LC/Monomer System

Fig. 2. Phase diagram of JB-5200xx/NOA73 monomer system before photopolymerization as obtained using optical microscopy. The symbol ϕ_{LC} represents the volume fraction of the liquid crystal.

before Polymerization

Figure 2 shows the experimental phase diagram as obtained by optical microscopy. The LC/monomer phase diagram is of the upper critical solution temperature (UCST) type, overlapping with the nematic-isotropic transition of the LC. Upon cooling the 92/8 mixture from an isotropic phase (100 °C) to a two-phase region, birefringence droplets appear below 68 °C, suggestive of nematic (N) and isotropic liquid (I) phase separation, as shown in Fig. 3 (left-hand images).

3.2 Morphology of LC/Polymer Composites after Photopolymerization: Effect of Temperature and UV Light Intensity

Temperature and UV light intensity both play an important role in the characteristics of the wall formation. Figure 3 shows transmission optical micrographs of the cells, placed between two crossed polarizers, made from the mixture formations with 8 wt% monomer samples at five different temperatures, dependent on UV illumination intensities, from 0 to 40 mW/cm^2 . The micrographs at 0 mW/cm^2 in Fig. 3 (left-hand images) show that the structures consist of an interpenetrating monomer network (i.e. isotropic phase) in an LC phase before UV light irradiation. The formation of this structure is attributed to temperature-induced phase separation. Application of a patterned UV irradiation resulted in a significant change in the phase-separated morphologies.

Fig. 3. Transmission optical micrographs of the cells made from the JB-5200xx/NOA73 (92/8) mixture formation showing the dependence of polymer-wall structure on temperature vs. UV light intensity after photopolymerization.

At temperatures below 42 °C, the low UV light intensity region produced insufficient of wall-structure and the material remained in the isotropic phase in internal pixels. A periodic dot pattern has been observed in the photopolymerization caused in the linewidth regions of photomask. Fine-continuous wall-structure has been observed with UV intensity increased to 40 mW/cm² below 40 °C or over 30 mW/cm² at 42 °C. These polymer walls are located in a lattice pattern, corresponding to the regions exposed through photomask. On the other hand, with the temperature at 45 °C, the low UV light intensity region exhibits the same result as that found below 42 °C, and fine-continuous wall-structure has been observed at an intermediate UV light intensity between 20 to 30 mW/cm². At the higher UV light intensity of 40 mW/cm², however, small domains with isotropic phase remain in internal pixels, similar to those in the lower UV light intensity region. Fine-continuous wall-structure could

not be confirmed under any UV intensity condition at temperatures above 48 °C.

3.3 Morphology of Local Photopolymerization

To mimic the dynamics of phase separation and structure development, optical microscope images of the phase-separated structures were observed under different irradiation conditions. Structural analysis was then performed on the acquired images by line profile. The local photopolymerization reaction induced by irradiating selective areas of a cell with UV light through the photomask was investigated by inspection of the line profiles of optical microscope images, observed under crossed polarizers. The results of the line profiles along the *y*-direction, corresponding to the spatially continuous light intensity region at a temperature of 40 °C, are shown in Fig. 4. In these figures, the vertical scale is the luminous level of the optical microscopic image. White and black levels can be regarded as LC and polymer regions, respectively. The lower UV

intensity region, below 25 mW/cm^2 , has a periodic dot pattern structure as shown above. The average wavelength λ of periodic dot pattern reduces with increasing UV intensity. Finally, the morphology of LC/polymer mixture shifts its structure from a dot pattern to a continuous wall at above 30 mW/cm^2 . Figure 5 shows the average wavelength of the periodic dot pattern, dependent on UV intensity. The

Fig. 4. Line profiles of the polymer-wall structure along the y -direction at 45°C : (a) 5 mW/cm^2 , (b) 10 mW/cm^2 , (c) 25 mW/cm^2 , and (d) 40 mW/cm^2 .

Fig. 5. Temporal change in the average wavelength of periodic dot pattern, dependent on UV intensity.

Fig. 6. SEM images of the polymer-walls at 45°C : (a) 10 mW/cm^2 , (b) 30 mW/cm^2 , and (c) 40 mW/cm^2 .

observed unique profile may well be connected with this reaction. From the data available, it is plausible to assume that the observed dot pattern profiles are induced by the spinodal decomposition type of phase separation [25-26] that is occurs where concentration fluctuations grow in the unstable conditions.

3.4 Polymer Wall Morphology

It is of interest to examine the morphology of the polymer wall after the extraction of the LC from the composite. In this experiment the UV intensity varied from 10 to 40 mW/cm^2 , while the curing temperature was fixed. The SEM images of samples with UV intensities of 10 , 30 , and 40 mW/cm^2 at a temperature of 45°C are shown in Fig. 6(a), (b), and (c), respectively. The results indicated that the wall density increases as the UV intensity increases, consistent with the observations made from optical microscopy. Low UV intensity, as shown in Fig. 6(a), resulted in insufficient wall-structure. In this case, it is understood that the small isotropic phase observed in the previous optical result is a monomer, because polymer particles are not observed in interpixel regions. Increasing the UV intensity, as shown in Fig. 6(b), produces a fine-continuous

Fig. 7. SEM images of the polymer-walls at 40 °C: (a) 5 mW/cm², (b) 10 mW/cm², (c) 25 mW/cm², and (d) 40 mW/cm².

wall-structure with sharp, smooth boundaries. Thus, solid and well-defined walls with sharp, smooth boundaries can be obtained by optimization of the UV intensity for phase separation at this temperature condition. A higher UV intensity, as shown in Fig. 6(c), resulted in an increase in the relative proportion of the polymer network in both the walls and interpixel regions. This differs from the low UV-intensity condition, where the interpixel regions were rich in LC regions, involved in droplet-like domains of polymers. This assumes that the free radicals that diffused from the high UV-intensity region and/or the residual monomer were polymerized in the non-UV-irradiation region.

Figure 7 shows SEM images of samples at UV intensities from 5 to 40 mW/cm² at a temperature of 40 °C. The polymer morphologies with UV intensity conditions below 25 mW/cm² have a periodic dot pattern structure. At the high UV-intensity of 40 mW/cm², fine-continuous polymer walls with approximate line and space dimensions

consistent with the photomask can be observed. These morphological results of polymer-walls agree well with the previous optical microscope investigations.

3.5 Diffusion Model for Photoinduced Formation of Polymer-Walls

From the above observation results, it is confirmed that the formation of the polymer-walls is strongly dependent on the fabrication conditions such as UV intensity and temperature. We now consider a phenomenological diffusion model to describe the kinetics of polymer-wall formation in LC/monomer mixtures, based on the reaction-diffusion model of holographic grating studies [27,28], applying conservation of mass results in Fick's second law. This model is a one dimensional diffusive transport equation for the monomer concentration φ_m :

$$\frac{\partial}{\partial t} \varphi_m = \frac{\partial}{\partial x} \left[D \frac{\partial \varphi_m}{\partial x} \right] - R_p \varphi_m. \quad (1)$$

The polymer concentration, φ_p , is given by

$$\frac{\partial}{\partial t} \varphi_p = R_p \varphi_m, \quad (2)$$

where the diffusion coefficient D depends on the φ_m . R_p is the polymerization rate, which is assumed to be proportional to the square root of incident intensity of UV light.[29] One may write:

$$R_p = \frac{k_p}{k_t^{1/2}} [\Phi I_o f(x)]^{1/2}, \quad (3)$$

where I_o is the intensity of incident UV radiation, k_p and k_t are the propagation and termination rate constants, Φ is the quantum yield (or photochemical efficiency), and x is the spatial parameter. For pattern photopolymerization one must account for the spatial variation of the reaction rate induced by the periodic UV intensity. $f(x)$ is the function of the spatial light-intensity variation pattern in the x -direction, i.e. $f(x)$ is a constant for a uniform polymerization process such as conventional PDLCs, or a sinusoidal function for non-uniform polymerization process such as holographic polymer-dispersed liquid crystal (H-PDLC).[30,31] For our non-uniform polymerization process to form polymer-walls, $f(x)$ is a periodic rectangular function in the x -direction, determining the regions where the

Fig. 8. Schematic illustration of the formation of polymer walls and model for the mechanism: (a) UV irradiation process, (b) periodic patterned UV region along the x-direction, and (c) continuous UV intensity region along the y-direction.

photoreaction rate varies periodically.

In polymer-walled cells formed by local polymerization-induced phase separation, spatial variations in the structure can be achieved by introducing non-uniform polymerization conditions (Fig. 8(a)). During the photopolymerization process, monomer migration is assumed to be driven by a chemical potential gradient. Photopolymerization of the monomer occurs preferentially in the UV-irradiation regions relative to that in the non-irradiation regions. In the irradiated region, more free radicals are produced, and the monomers become polymerized to form polymers. The consumption of monomers in these regions lowers their chemical potential. This induces the monomers to diffuse from the non-irradiation regions to the irradiation

regions. On the other hand, the LC molecules diffuse from the irradiation to non-irradiation regions in order to balance the chemical potential. As a result, the LC is squeezed out of irradiating regions. Finally, As a consequence, a concentration gradient develops in the mixtures, thereby forming LC-rich layers alternating periodically with polymer-rich layers as shown in Fig. 8(b). Two competing processes are apparently involved: diffusion and LC/polymer phase separation during polymerization. These two processes have different temperature and UV-intensity dependences. At lower temperatures the two processes occur at very significantly different rates where, perhaps, the phase separation rate (or polymerization rate) is much faster than diffusion. The lower UV-intensity exposure causes a slower phase separation which leads to periodic dot pattern structure induced by the unstable condition (i.e. spinodal decomposition), as shown in Fig. 8(c). After polymerization, the polymer structure dramatically reduces diffusion speed, and leads more uncured monomers in the masked area. On the other hand, at high temperatures or high UV-intensities, both diffusion and phase separation processes are rapid, resulting in a more desirable structure of polymer wall. This suggests the existence of a range of suitable curing intensities, experimentally supported by the fact that an optimal value of curing intensity exists.

4. Conclusion

In this study, a method has been presented for formation of polymer walls using patterned UV irradiation, and it has been demonstrated that the phase diagram of mixtures of nematic LC and reactive monomer is of the UCST type, overlapping with the nematic-isotropic transition of the LC. Large amounts of polymer diffuse from the pixel area resulting in large domain LC texture, which improves the brightness, contrast ratio, and other electro-optic characteristics of the LC devices. Both diffusion and phase separation processes are involved in the polymer wall formation. Upon exposure to UV light, the monomer migrates from the masked area to the exposed area. Temperature has significant effect on the character of the wall formation. This is readily apparent from an examination of the SEM

pictures. Formation, curing temperature, UV intensity, exposure time, and the ratio of the exposed area to the masked area all affect the wall formation process. Further experiments are in process to control and optimize these factors.

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